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Synergistic effect of the parameters affecting wet flue gas desulfurization using magnesium oxides by-products

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HIGHLIGHTS

- The effect of Mg is greater than that of Ca in the desulfurization process.
- The pH limit for 100% removal efficiency is over 4 regardless the FGD technology.
- A combined effect of solid (*S*) and water (*W*) on efficiency showed two behaviors.
- Addition of *S* in the low *S*/*W* range has a positive effect over efficiency.
- Addition of *S* at higher *S*/*W* values has a negative effect.

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ABSTRACT

A previous study carried out by the authors allowed to identify the optimum MgO by-product for a 100% SO_2 removal efficiency in a wet flue gas desulfurization (FGD) process. The present research analyzes the synergistic effect between the main parameters affecting the proposed desulfurization process. The design of experiments (DoE) was used as statistical tool for evaluating the influence of the solid-to-water ratio (*S*/*W*), water (*W*) and time of reaction (t_R) over the most important responses of the FGD process: Mg^{2+}, Ca^{2+} and SO_4^{2-} in solution, pH and conductivity (k), and time of saturation (t_S). According to the analysis performed, the results of Mg^{2+} and Ca^{2+} leaching showed the greater effect of Mg compounds. The production of SO_4^{2-} was simultaneously affected by *S*/*W* and *W*, due to the mass-transfer nature of the process. The pH range was found to be controlled by the solubility product of the alkaline phases while k showed a linear dependency on the dissolution of the solid and SO_2 absorption. As for desulfurization efficiency, two behaviors were observed by the combined effect of the factors: low *S*/*W* ratios in the whole *W* range showed that adding more solid had a positive effect as it increased t_S while higher ratios decreased it. Hence, an optimum *S* and *W* consumption for 100% removal efficiency can be estimated in sake of saving energy, *W* and by-product. The present research methodology could be extended to other by-products for wet FGD as the current EU legislation is driving the industry to the reutilization of wastes and residues.

1. Introduction

Sulfur dioxide is emitted from anthropogenic sources when fuels containing sulfur are burned. Once in the atmosphere it is oxidized to sulfur trioxide and further solubilized in water to form sulfuric acid rain [1]. Among its major consequences, affections to the respiratory system and acidification of soils and aquatic ecosystems stand out because of their damaging effects [2]. Thus, the European Community imposed in the past very strict regulations (88/609/CEE and 2001/80/CEE Directives) for the sulfur dioxide content in the flue gases released from the fossil-fuel combustion and the metallurgical and oil-refining industries [2]. As a response, EU SO_x emissions have decreased a 46% [3]. In order to achieve removal of SO_2 and fulfill the environmental legislation limits, flue gas desulfurization (FGD) technologies have been applied since the 1970s and nowadays the methods employed are very advanced [4,5]. In this aspect, FGD processes can be roughly divided in three kinds: pre-combustion, combustion and post-combustion technologies. The existing pre-combustion desulfurization processes include physical, chemical and biological cleaning for coal that are not currently practical to adopt, as they use costly chemical and catalysts [1]. Combustion processes generally include the injection of the absorbent in the combustion area, with ground limestone being

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Nomenclature

L/G	liquid to gas ratio (liters of slurry per m^3 of gas)
t	time (min)
W	mass of water (g)
S	mass of by-product (g)
L	mass of slurry (g)
S/W	solid-to-water ratio (wt%)
t_S	saturation time (min)
t_R	time of reaction (min)
f	gas flow (L min^{-1})
ρ_s	density of the slurry (kg L^{-1})

the most commonly used [6]. Accordingly, the major technologies to control SO_x emissions are based on post-combustion controls, which in turn can be classified as once-through or regenerable [7]. In once-through technologies, the SO_2 is predominantly bound in the sorbent, which must be disposed of as a waste or utilized as a by-product (e.g., gypsum). As for the regenerable type, no waste is produced. Both can be further classified as either wet or dry depending on the moisture content of the resulting residual material [8]. Wet FGD technologies have been predominantly selected over others because of the high desulfurization efficiency, high utilization rate of reagents and a stable operating environment [8–12]. More specifically, the dominating wet FGD technology is absorption of SO_2 in a limestone slurry because of its natural abundance and low cost [12,13].

However, the tighter regulations imposed in the Industrial Emissions Directive (2010/75/EU) into force at the beginning of 2011 through the Best Available Techniques (BAT) reference document have lead the research over the abatement of SO_2 emissions to technologies that could fulfill a 100% removal efficiency by reusing or recycling residues and wastes. This fact has fostered the different industries involved to achieve emissions control by means of sustainable methods that include the use of low-waste technologies and the recovery and recycling of the substances generated. Thus, it can be stated that the primary targets of the research over wet FGD are currently the attaining of a 100% removal efficiency by reusing wastes or recycled materials [14]. In the framework of this issue, the authors have already studied the suitability of different by-products from the calcination of natural magnesite as desulfurization agents in a wet FGD batch discontinuous reactor [15]. These by-products are usually referred to as Low-Grade magnesium (hydr)oxide (LG-MgO/$Mg(OH)_2$) and are characterized for being a mixture of mainly magnesium (hydr)oxides and different proportions of calcium (hydr)oxides, dolomite and siliceous materials, altering their alkaline behavior and therefore their acid neutralization capacity (ANC) [16]. The results obtained from this study allowed determining the most suitable by-product (~68 wt% MgO) and the average consumption (2.9 kg of solids per Nm^3 of SO_2) for 100% removal efficiency. This value is approximately three times the consumption of the widely used high-grade lime in the same conditions [15]. For this MgO by-product, the minimum pH range for assuring total SO_2 neutralization at industrially interesting liquid-to-gas (L/G) ratios was determined to be 5.2–6.3, in accordance with other similar studies considering other absorbents and different technologies [17,18]. Likewise, the initial approach carried out in the past study also allowed identifying the main parameters affecting the performance of this by-product as desulfurization agent as well as the range of action for practical purposes at industrial scale. These parameters can be described as follows. Firstly, the double effect of magnesium and calcium compounds in the solid promoted dissolution (Mg^{2+} and Ca^{2+}) and hence desulfurization effect in a particular manner, which is distinctive of this kind of by-products [15,16]. The enhancement of lime and limestone FGD process by adding magnesium attracted much interest in the past few years because the greater solubility of magnesium salts allowed to increase the dissolved alkalinity and consequently the SO_2 removal [19,20]. By this manner, lower recirculation and energy requirements could be obtained. Besides, magnesia scrubbing process has the competitive advantage of solving the problem of solid by-product disposal when $MgSO_4{\cdot}7H_2O$ is controlled as the main by-product and regenerated for reuse as the absorbent [20,21]. Secondly, pH is regarded to be the main operating parameter for minimizing operation costs [11,18,22,23]. This variable is directly related to the ANC of the by-product and hence to the presence of different buffering phases, such as alkaline hydroxides and carbonates [16]. The abovementioned factors (Mg^{2+}, Ca^{2+} and pH) are directly related to the quantity of solid (S) dissolved in water (W), both amounts (g) integrated in a solid-to-water (S/W) ratio. The efficiency of the process has been reported to be dependent on the solid used in the preparation of the absorbent suspension as well as to the water involved in the mass-transfer process [9,15,24]. A similar influence to the mass-transfer process can be deduced from the liquid-to-gas (L/G) ratio, which is considered one of the most important parameters for describing the desulfurization process as the dissolution process of the solids and thus the absorption of SO_2 is controlled by mass transfer [5,11,17,18,21,22]. In a batch reactor at lab-scale, this ratio is defined by the quantity of slurry put in contact with the gas while at larger scales, such as in a packed column scrubber, is defined by the recycle's pump power [5]. Controlling the course of reaction during a continuous desulfurization process has to be done by considering parameters that are practical to understand and easy to measure, like pH and conductivity (k). The latter is obviously related to the presence of the major dissolved cations (mainly Mg^{2+} and Ca^{2+} among others) and anions (SO_4^{2-} and sulfur related species). For this reason, k was identified as a key controllable parameter. In addition, and in order to evaluate complete removal efficiency, the authors introduced the *saturation time* (t_S) defined as the time where no SO_2 is detected in the treated gas at the outlet and allows considering 100% removal efficiency. Hlincik and Buryan utilized a similar concept for evaluating the reactivity of two different limestones although their emission limit or breakthrough point for SO_2 concentration at the outlet was set at 200 mg Nm^{-3} [10].

Therefore, there are several parameters that have to be considered when studying the desulfurization potential of by-products, especially when these are a complicated mixture of different compounds with a different behavior in the whole pH range of study. As a consequence, in order to completely understand the chemical process taking place during the use of these by-products as desulfurization agents, the synergistic effect between parameters ought to be assessed and the influence of each parameter over the rest has to be evaluated collectively. To carry this on, conventional individual experimental designs are not useful as they cannot considered which parameter is dominant or how significant it is [25]. The research over the optimum operating parameters in wet limestone FGD has been extensively studied by means of one-dimensional models [22], and there is scarce literature over the potential interactions between parameters. In this aspect, Zhao